Methane-derived authigenic carbonates from the northern Gulf of Mexico and their relation to gas hydrates

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Abstract

Authigenic carbonates were sampled in piston cores collected from both the Tunica Mound and the Mississippi Canyon area on the continental slope of the northern Gulf of Mexico during a *Marion Dufresne* cruise in July 2002. The carbonates are present as hardgrounds, porous crusts, concretions or nodules and shell fragments with or without carbonate cements. Carbonates occurred at gas venting sites which are likely to overlie gas hydrates bearing sediments. Electron microprobe, X-ray diffraction (XRD) and thinsection investigations show that these carbonates are high-Mg calcite (6 - 21 mol % $MgCO_3$), with significant presence of framboidal pyrite. All carbonates are depleted in ^{13}C ($\delta^{13}C$ = -61.9 to -31.5 ‰ PDB) indicating

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that the carbon is derived mainly from anaerobic methane oxidation (AMO). Age estimates based on ^{14}C dating of shell fragments and on regional sedimentation rates indicate that these authigenic carbonates formed within the last 1,000 yr in the Mississippi Canyon and within 5,500 yr at the Tunica Mound. The oxygen isotopic composition of carbonates ranges from +3.4 to +5.9 ‰ PDB. Oxygen isotopic compositions and Mg^{2+} contents of carbonates, and present *in-situ* temperatures of bottom seawater/sediments, show that some of these carbonates, especially from a core associated with underlying massive gas hydrates precipitated in or near equilibrium with bottom-water. On the other hand, those carbonates more enriched in ^{18}O are interpreted to have precipitated from ^{18}O-rich fluids which are thought to have been derived from the dissociation of gas hydrates. The dissociation of gas hydrates in the northern Gulf of Mexico within the last 5,500 yr may be caused by nearby salt movement and related brines.

Keywords: methane-derived authigenic carbonates; Gulf of Mexico; high Mg-calcite; carbon and oxygen isotope; age of authigenic carbonates; dissociation of gas hydrates

1. Introduction

The co-occurrence of authigenic carbonates and gas venting has been documented at many gas hydrate sites [e.g., the Blake Ridges (Naeher et al., 2000), the Cascadia Margin (Bohrmann et al., 1998), the Gulf of Mexico (Saseen et al.,

2004)]. In these areas the carbon in the carbonates was mainly derived from methane. Thus carbonate precipitation may be related to the decomposition of gas hydrates.

Determining the age of authigenic carbonate formation is difficult. Some researchers hypothesized that the gas hydrate related authigenic carbonates formed during the Last Glacial Maximum (LGM) (Bohrmann et al., 1998; Aloisi et al., 2000). However this interpretation assumes that the lowered sea level during the Pleistocene, and reduced pressure on the ocean margins triggered gas hydrate dissociation.

Because ^{14}C datable shell fragments were mixed with some sampled authigenic carbonates in the northern Gulf of Mexico, some chronological control is available that helps constrain the time of formation of these authigenic carbonates. High-resolution seismic profiles across the core sites and regionally well known sedimentation rates (Coleman et al., 1983; Rowan and Weimer, 1998) also help constraints on the time of formation of carbonates.

Here we present geochemical data for carbonates recovered from piston cores obtained in sediments from the northern Gulf of Mexico (Fig. 1). The data document variations in the carbon and oxygen isotopes, chemical compositions, mineralogy and the timing of the carbonate precipitation. The carbon isotopic values suggest carbonate carbon is derived from anaerobic oxidation of methane. The variations in oxygen isotopes together with other geochemical proxies provide the evidence for relationship between the authigenic carbonate and the gas hydrates.

2. Geological background and sampling

The northern Gulf of Mexico is a passive continental margin characterized by over 10 km thick Mesozoic-Cenozoic sediments, which are well-suited for the generation and accumulation of large oil and gas reservoirs. The extensive salt deposits and salt thrusts within this margin provide an excellent environment for both hydrocarbon accumulation and migration (Sassen et al., 1994). During the Late Triassic, rifting of the Gulf of Mexico led to the formation of many sub-basins; these basins were then floored by thick salt (Louanne/Werner formations) during Middle Jurassic marine incursions (Salvador, 1987) and formed the main structural features of the northern Gulf of Mexico. Since the Cenozoic, the long history of ongoing salt diapirism has resulted in structural deformation, faulting, fracturing and sediment slumping, all of which provide conduits for upward seepage of gaseous and liquid hydrocarbons. Authigenic carbonate minerals and gas hydrates on the seafloor and within sediments are the cumulative products of these extensive hydrocarbon seeps (e.g. Brooks et al., 1984, Roberts and Aharon, 1994). Authigenic carbonates are so pervasive in this region that carbonate mounds and hydrate-related hills can exceed a kilometer in diameter (Nerauter and Roberts, 1992). These authigenic carbonates may cap gas hydrates bearing strata and provide a temporal record of hydrocarbon seeps.

During July 2002, *Marion Dufresne* Cruise MD-02 investigated the occurrence and distribution of gas hydrates in the shallow subsurface from the upper continental slope of the northern Gulf of Mexico using the giant Calypo piston corer. Authigenic carbonates were recovered from different sub-depths between 0 and 27 mbsf in sediments at the Tunica Mound, on the floor of the Mississippi Canyon and to the

west of the Mississippi Canyon (Fig.1). Before this cruise, carbonate samples had been recovered only from near surface sediments using submersibles in the Gulf of Mexico (Robert and Aharon, 1994; Aharon et al., 1997).

The authigenic carbonates investigated in this paper came from several different geological environments: (1) on or near seafloor sediments on the crest of a salt diapir at the Tunica Mound (the cores MD02-2543G, 2544G, 2545G), (2) in shallow sediments over a gas chimney (MD02-2570, 2571C2) to the west of the Mississippi Canyon, (3) at up to 27 mbsf sediments near the salt diapir at the Tunica Mound (MD02-2546), and (4) in sediments associated with gas hydrates (MD02-2569 and MD02-2573GHF) (Fig. 2 and Fig. 4) on the floor of the Mississippi Canyon.

3. Methods

The carbonates (n = 25) were examined in hand samples, petrographically and geochemically. Bulk mineralogy (n = 35) was determined on pressed powder mounts using a Mac Science MXP3 Powder X-ray Diffractometer (XRD) at University of Tokyo. The XRD patterns were obtained from 0º to 40º 2θ at a scanning speed of 2º 2θ/min. The weight percentages of minerals were estimated using the peak weights (Müller, 1967) with an estimated error of ±5 %. Carbon-coated, polished thin sections were made from selected authigenic carbonates and examined by electron microprobe analyses using a JEOL Superprobe 733 – II to provide detailed chemical compositions of calcite. Concentrations of Ca, Mg, Mn, Fe, Sr, and Ba were determined. The analytical precision is 1% for Ca, 2% for Mg, 4% for both Fe and Mn, and 9% for

both Sr and Ba.

Oxygen and carbon isotope compositions (n = 34) were measured on the same set of samples examined by XRD, CO_2 gas was produced by reaction with 100% phosphoric acid at 25 ºC for 24 hours and the purified CO_2 gas was analyzed using a Finnigan MAT 252 Mass Spectrometer at University of Tokyo. The isotopic compositions are given relative to the Peedee Belemnite (PDB) reference, with a precision of ±0.2‰ for both $\delta^{13}C$ and $\delta^{18}O$ values.

Pore waters for stable oxygen isotope analysis were collected by squeezing 10 cm long, whole-round core sections at about 3 m intervals in the cores (Ussler and Paull, 2005). Oxygen isotopic compositions of 155 pore waters was determined using the H_2O-CO_2 equilibration method (Epstein and Mayeda, 1953). The resulting CO_2 was purified and collected by cryogenic transfer. Stable oxygen isotope ratios of CO_2 were also measured on a Finnigan MAT 252 mass spectrometer at University of Tokyo. Oxygen isotope measurements on the pore waters are reported in the standard δ notation with respect to Standard Mean Ocean Water (SMOW). The cumulative (vacuum line and mass spectrometer) accuracy and precision of oxygen isotopic measurements are ±0.2‰, and ±0.06‰ respectively.

The ^{14}C measurements were made on shell fragments with and without carbonate cements (n=2) in the core MD02-2543G. To remove contaminants, the shell fragment was carefully stripped off adhering sediments under a microscope, repeatedly placed into Milli-Q water in an ultrasonic bath and leached using lM HCl. The washing was finished with a final rinsing with Milli-Q water, and the sample was dried in a

desiccator in a vacuum line. Under vaccum, the shell was reacted with phosphoric acid and the evolved CO_2 was reduced to get graphite targets prepared following the method described by Miyairi et al. (2004). The ^{14}C concentration was measured using accelerator mass spectrometry (AMS) in a Pelletron 5UD Tandem accelerator at the Research Center for Nuclear Science and Technology, University of Tokyo. The analytical precision was ±0.5%. The age was calculated as years before present (BP, years from AD1950), and errors are expressed as ± 1σ.

4. Results

4.1 Occurrence of authigenic carbonates

Authigenic carbonates were collected at the Tunica Mound in cores MD02-2543G, 2544G, 2545G and 2546 with water depths ranging between 579 m and 595 m. The geothermal gradient was measured to be 29 °C/km, with a bottom water temperature of 7.1 ºC at these sites (Geli et al., in prep.). Seismic profiles from this site (Fig. 2) show that Tunica Mound is underlain by a large salt diapir. The authigenic carbonates were found at the top of the core MD02-2543G and occurred as broken pieces of hardgrounds, with or without carbonate cemented shell fragments being present (Fig. 3). Carbonates recovered from the core MD02-2544G, consisted of porous crusts with non-cemented shell fragments (Fig. 3) on the seafloor. One big hard and irregularly shaped concretion was obtained at 4.25 mbsf in the core MD02-2545G (Fig. 3). A semi-consolidated concretion, with a small cemented shell

fragment was at ~ 27 mbsf in the core MD02-2546. That concretion is the deepest one recovered during this cruise (Fig. 3). No gas hydrates were found or inferred to have existed in any of the cores taken at the Tunica Mound (Paull et al., submitted), however this area is characterized with gas venting.

The authigenic carbonates were also recovered from two cores (MD02-2569 and 2573GHF) on the floor of the Mississippi Canyon in the gas hydrate area, at a water depth of 1027 m and bottom water temperature of 4.6 ºC (Fig. 4). Both cores were observed to contain gas hydrates. Carbonates in MD02-2569 occurred as irregular hard nodules in sediments just below the seafloor, underlain by two layers of massive gas hydrates (Fig. 4). One layer occurred at ~ 3 mbsf, as a chunk of gas hydrate filling the entire 10 cm diameter core liner (Fig. 5). Carbonates in core MD02-2573GHF were found coexisting with small pieces of gas hydrates, distributed as porous concretions in irregular shapes (Fig. 5).

The authigenic carbonates recovered in the cores MD02-2570, 2571C2, are near to a gas chimney at the west of Mississippi Canyon (Fig. 4), 628 m in water deepth, with a bottom water temperature of 6.5 ºC, and a geothermal gradient of 36 °C/km (Geli et al., in prep.). In core MD02-2570, round semi-consolidated carbonates nodules were obtained in sediments at ~ 3 mbsf. While the carbonates in the core MD02-2571C2, were ~35 cm thick, and occurred as semi-consolidated nodules and slabs. One ~2 cm thick carbonate slab has a round hole of ~ 0.5 cm in diameter, which may be the conduit for gas venting (Fig. 5).

In summary, most of the authigenic carbonate samples occurred on the seafloor

or in shallow sediments, (i.e. ≤ 5 mbsf) surrounding gas vents, except for one sample obtained at ~ 27 mbsf in the core MD02-2546.

4.2 Petrography and mineralogy

Observations of thin sections showed that the predominant micritic authigenic carbonates were developed within fine-grained clastic sediments. Silt sized quartz grains, formanifera (mostly are planktonic), bivalve shell fragments and framboidal pyrites were noted as well as numerous cavities. The cavities were cemented with micritic carbonates, organic matter and some frambodial pyrites. In only one sample (MD02-2544G) barite was identified (≤ 5%) (Fig. 6).

Thirty-one authigenic carbonates and one bivalve shell were analyzed by XRD. The samples are primarily composed of calcite and quartz with subordinate amounts of dolomites and pyrites. Calcite content ranges from 41 wt% to 94 wt%, with a mean of 73 wt%. Differences among crust, hardground and nodule in mineralogy by area are not obvious.

The position of the major diffraction peak *d*(104) of calcite varies between 2.978 and 3.014 Å (Fig. 7). The shift of *d*(104) values away from that of stoichiometric calcite (3.035 Å) is caused by substitution of Mg^{2+} for Ca^{2+} , as well as by other divalent ions. Most calcites centered around 2.998 Å, indicating an $MgCO_3$ content of approximately 12 mol% based on the standard calibration curves from Müller (1967). However two extremes of calcite *d*(104) measured roughly show a range of $MgCO_3$

content in calcite from 6 mol% to up to 20 mol%.

4.3 Geochemistry

4.3.1 Chemical compositions of calcite

Seventeen authigenic carbonate samples were measured by electron microprobe. The data show that all carbonates are high magnesium calcite, with 6 to 21 mol% Mg^{2+} (Table 1), which are consistent with the shifts of *d*(104) determined by XRD analysis. These carbonates also contain minor amounts of FeO and MnO (Table 1), which indicates carbonates have precipitated in reducing environments.

4.3.2 Stable carbon and oxygen isotopic compositions of carbonates

Stable isotopes of carbon and oxygen were measured on 23 bulk authigenic carbonate samples and on 11 microdrilled samples from carbonate nodules in the cores MD02-2545G, MD02-2569 and MD02-2571C2 A20-25cm (Table 2). Except for the shell fragment ($\delta^{13}C_c$ = -3.1 ‰), all the carbonates are extremely depleted in ^{13}C, with $\delta^{13}C_c$ values ranging from -35.8 ‰ to -61.9 ‰. The oxygen isotopes of carbonates ($\delta^{18}O_c$) range from +3.4 ‰ to +5.9 ‰ (Table 2, Fig. 8).

4.3.3 Stable oxygen isotopic compositions of interstitial water

Because except the carbonates in the core MD02-2546, all sampled carbonates

occurred in the upper 5 m sediments, the stable oxygen isotopic values of interstitial water ($\delta^{18}O_{IW}$) from the upper 6 m sediments were taken into account in this study. These $\delta^{18}O_{IW}$ values almost remain constant with depth for the upper 6 m in each core, and most of them (n=30 out of 34) range from +0.7 ‰ to +1.0 ‰, with a mean of +0.8‰. Thus we can regard these $\delta^{18}O_{IW}$ values reflecting the regional bottom seawater oxygen isotope ($\delta^{18}O_{sw}$), with the exception of 4 samples in the core MD02-2543G, which have values ranging from -0.6 ‰ to -0.4 ‰. These samples came from the upper 0.15 mbsf and were the only sediments obtained in the core which was apparently bent. The negative $\delta^{18}O_{IW}$ values may have been caused by diagenetic reactions at low temperatures with the underlying patchy tephra in the core. Because the carbonates in the core MD02-2543G were just below the seafloor, we will assume $\delta^{18}O_{IW}$ values of these carbonates are the same as the regional $\delta^{18}O_{sw}$.

There was no interstitial water available for $\delta^{18}O$ analysis in the cores MD02-2544G, 2573GHF and 2571C2, due to no sediments recovered. The carbonates in these cores occurred at the upper 5 m of sediments, thus we assume that $\delta^{18}O_{IW}$ values of the host sediments are the same as the regional $\delta^{18}O_{sw}$ values. The $\delta^{18}O_{IW}$ value of the pore water sampled from same horizon that contained the carbonates at ~ 27 mbsf in the core MD02-2546 is + 1.3 ‰.

4.3.4 ^{14}C ages of shells

The result of ^{14}C analysis shows that the shell and carbonate cemented shell in the core MD02-2543G have $\Delta^{14}C$ = -361.1 ± 4.7 ‰ ($\delta^{13}C$ = -3.1 ‰), and $\Delta^{14}C$ = -499.5 ± 5.0 ‰ respectively. Based on the conventional ^{14}C age calculation (Stuiver and Polach, 1977), these two shells may have ages of 3,600 ± 60 yr BP and 5,560 ± 80 yr BP respectively.

5. Discussion

5.1 Carbon isotopic variations of carbonates

The sources of carbon in the pore fluids in the Gulf of Mexico include: (1) methane ($\delta^{13}C$ = -120 ‰ to -30 ‰), (2) oil fractions ($\delta^{13}C$ = -25 to -28 ‰) (Aharon et al., 1997), (3) sedimentary organic matter ($\delta^{13}C$ = -25 ‰ on average), (4) marine biogenic carbonate ($\delta^{13}C$ = ~ 0 ‰)and (5) seawater CO_3^{2-} with a $\delta^{13}C$ value of $\delta^{13}C$ = 0±3 ‰ (Anderson and Arthur, 1983).

In order to identify the carbon source and the carbonate forming mechanism for the authigenic carbonates, carbon isotope analyses were carried out on the same sub-samples, which were also analyzed mineralogically. Because carbonate carbon isotope values (from -35.8 to -61.9 ‰) are lower than those found in any known carbon sources other than methane, they indicate that methane is the major carbon source of the carbonates. Supporting this conclusion is the occurrence of framboidal pyrite in these carbonates which requires anoxic conditions. Thus these carbonates were probably formed near where anaerobic methane oxidation (AMO) via sulfate

reduction occurred. One of the effects of AMO is to generate HCO_3^-, and to increase the alkalinity of the pore fluids, which contributes to the precipitation of authigenic carbonates. Moreover the addition of methane carbon to the pore fluid DIC (dissolved inorganic carbon) pool, which decreases the $\delta^{13}C$ value of the DIC, and may result in authigenic carbonates with low $\delta^{13}C$ values (Paull et al., 1992; Greinert et al., 2001). In contrast, the carbon isotope values of the shells are much higher (-3.1 ‰), suggesting that their carbon came mainly from seawater bicarbonate.

Two general mechanisms generate methane in the marine environment: microbial methane formed via CO_2-reduction and thermogenic-methane generated during organic matter maturation (Bernard et al., 1978; Whiticar, 1999).The $\delta^{13}C$ values of microbial methane are typically < -60 ‰. Conversely, thermogenic methane with the $\delta^{13}C$ values that are typically > -50 ‰ (Bernard et al., 1978).

According to the $\delta^{13}C_c$ values of -35.8 ‰ to -61.9 ‰, carbonates can be classified into two groups – Group I ($\delta^{13}C_c$ = -35.8 to -49.7 ‰) and Group II ($\delta^{13}C_c$ = -59.4 to -61.9 ‰) (Fig. 8). Group I carbonates were found at all the cores MD02-2543G, 2544G and 2545G except one core MD02-2546 at the Tunica Mound, and at both cores (MD02-2569 and 2573GHF) containing gas hydrates on the floor of the Mississippi Canyon. At the Tunica Mound, carbonate $\delta^{13}C_c$ values range from -35.8 ‰ to -49.7 ‰ with a mean of -42.6 ‰. At the floor of the Mississippi Canyon, the carbonate $\delta^{13}C_c$ values are in a tight range of -41.9 ‰ to -45.8 ‰ with a mean of -44.0 ‰. Group II carbonates were recognized in both cores (MD02-2570 and 2571C2) near a gas chimney at the west of the Mississippi Canyon and a core

MD02-2546 at the flank of the Tunica Mound. The carbonate $\delta^{13}C$ values range from -59.4 to -61.9 ‰, with an average of -60.3 ‰.

The distinction in the carbon isotopic values into group I (-35.8 to -49.7 ‰) and II (-59.4 to -61.9 ‰) may reflect the variation in the source of the methane carbon particularly origin of methane carbon comes from thermogenic or microbial sources. The group II values clearly indicate microbial methane carbon dominates in the carbon in the DIC pool from which the carbonates precipitated. However the group I carbonates may be coming from either primarily thermogenic methane sources or may indicate more dilution of the DIC pool with carbon from other sources, e.g. microbial methane carbon diluted by sea water DIC, or mixture of microbial and thermogenic methane carbon etc.. Localized conduits, e.g. faults/fractures caused by the salt movement for migration of thermogenic hydrocarbons from great depth in the sedimentary section to seafloor are common in the Gulf of Mexico, such as those recognized at the Tunica Mound as shown in Fig. 2.

5.2 Ages of carbonates

The age of the authigenic carbonates can be estimated from known regional sedimentation rates and/or ^{14}C measurements of associated shells.

Tunica Mound: Carbonates at the Tunica Mound are from Garden Banks Block 386 (GB 386). In this area, the sedimentation rate is 7-11 m/ka (1 ka = 1,000 yr) for the upper sedimentary section (Rowan and Weimer, 1998; Cooper and Hart, 2003). The carbonates in the core MD02-2546 occurred at around 27 mbsf in the stratified

sediments inferred from the seismic profile (Fig. 2). If constant sedimentation rates are assumed, this would suggest the nodule could be only 4,000 yr old.

Carbonates recovered from the cores – MD02-2543G, 2544G and 2545G, occurred on the top of the Tunica Mound. Because erosion is occurring here, the sedimentation rates cannot be used to determine the sediment ages. Fortunately shell fragments were also recovered together with these carbonates (Fig. 3). The ^{14}C measurements of the shell and carbonate cemented shell in core MD02-2543G, yield calculated ages of 3,600 ± 60 yr BP, and 5,560 ± 80 yr BP, respectively. These calculated ages suggest the carbonate cemented shell is around 2,000 yr older than the shell without cements. Because the top of the Tunica Mound is believed to be experiencing erosion, shells of different ages may be in close proximity. Moreover the apparently older carbonate cemented shell may have survived longer because it was protected from erosion due to the carbonate cemented cover. Authigenic carbonates from other cores – MD02-2544G and 2545G are very near to MD02-2543G, just on the top of the Tunica Mound, thus are likely to be of similar ages, younger than 5,500 yr.

Mississippi Canyon: The authigenic carbonates in the Mississippi Canyon occurred from the seafloor down to 4.6 mbsf in the stratified sediments shown by the seismic profiles (Fig. 2). Therefore we can use the known sedimentation rates to constrain the ages of the authigenic carbonates in these sediments. The average sedimentation rates at the upper slope of the Mississippi Canyon are up to 15-20 m/ka due to sediment instabilities during the last 20 ka (Coleman et al., 1983). Since the

carbonate concretions in the sediment can not be older than the sediment deposits, the carbonates probably precipitated in Recent times, and are less than 1,000 yr ago.

In summary, all the authigenic carbonates collected during this cruise precipitated very recently, younger than 5,500 yr in the Tunica Mound, and less than 1,000 yr ago in the Mississippi Canyon.

5.3 Oxygen isotopic variations of carbonates and gas hydrate dissociation

The oxygen isotopic composition of any particular sample of authigenic carbonates is controlled by a combination of factors including: (1) sample mineralogy and chemistry, (2) temperature of carbonate precipitation and, (3) pore fluid isotopic composition (Anderson and Arthur, 1983). To investigate whether the analyzed $\delta^{18}O$ values of the carbonates are in equilibrium with ambient waters or not, and what factors are critical to the $\delta^{18}O$ of the authigenic carbonates, the following oxygen isotope fraction equations were used.

Mg-calcite: $1000\ln\alpha = 2.78 * (10^6/T^2) - 2.89 + 0.06 *$ mol % $MgCO_3$ (Friedman and O'Neil, 1977)

Aragonite: $t = 19.9 - 4.34 * [\delta^{18}O_{arag\ (PDB)} - \delta^{18}O_{w\ (SMOW)}]$ (Hudson and Anderson 1989)

In these equations, $\alpha = \dfrac{1030.91 + 1.03091 * \delta^{18}O_{c(PDB)}}{1000 + \delta^{18}O_{w(SMOW)}}$ representing the oxygen isotope fractionation between the carbonate and the water in which it precipitated; T is the absolute temperature (^oK); and t is the centigrade temperature (^oC).

According to ^{14}C dating and sedimentation rates, authigenic carbonates collected

during this cruise have precipitated within the last few thousand years. Therefore influence of the last glacial-interglacial cycles on bottom seawater temperatures and oxygen isotopes can be ignored. Thus present *in-situ* bottom seawater temperatures can represent the bottom water temperatures at which these authigenic carbonates have precipitated.

Due to the authigenic carbonates have precipitated originally in the sediments between the present bearing depths and the seafloor, we can estimate the possible temperatures at which these carbonates have precipitated according to the heat flow data measured by French PAGE group (Geli et al., in prep.). Using these temperatures, the $\delta^{18}O_w$ of the water in equilibrium with these carbonates can be calculated.

Tunica Mound: Because bivalves live on the seawater. For shell fragments we can assume that they were formed at the same temperature as the present bottom water temperature. The $\delta^{18}O$ of water for the formation of shell in the core MD02-2543G was calculated to be +0.7 ‰, using present bottom seawater temperature 7.1 ºC. This is in good agreement with the measured regional $\delta^{18}O_{sw}$ (Fig. 9).

The carbonates in the cores MD02-2543G and 2544G are believed to be exposed on the seafloor by erosion and there is no geothermal gradient measured for the core MD02-2545G. We assume that present bottom water temperature 7.1 ºC represent the temperature these carbonates formed. The theoretical $\delta^{18}O_w$ values for these carbonates at the Tunica Mound were calculated from +0.9 to +1.1 ‰, close to the measured present regional $\delta^{18}O_{sw}$ (Fig. 9). Therefore, it is reasonable to infer that

these carbonates from the Tunica Mound precipitated in or near isotopic equilibrium with present regional bottom water, and also confirm that carbonates in the cores MD02-2543G, 2544G and 2545G have originally precipitated in very recent times in the shallow sediments.

For the carbonate nodule in the core MD02-2546, we assume that the nodule was precipitated in the sediments not deeper than the present sub-depth (~ 27 mbsf). Therefore the nodule precipitated at between present bottom seawater temperature (7.1 ºC) and subsurface temperature (7.9 ºC) which was estimated from the heat flow data. Then the calculated $\delta^{18}O_w$ values for carbonate in the core MD02-2546 are from +2.7 ‰ to +2.5 ‰, which are much higher than those of the present observed pore water (+1.3 ‰) or the present bottom water (+ 0.7 ‰) (Fig. 9).

Mississippi Canyon: Authigenic carbonates in the core MD02-2569 in the seafloor sediments are underlain by two horizons of massive gas hydrate at 3 mbsf and 6 mbsf repectively. The bottom water temperature of 4.6 ^{o}C suggests carbonates precipitated from water with an oxygen isotope composition of +0.7 ‰, which is in good agreement with present $\delta^{18}O_{sw}$ (Fig. 9). Therefore, carbonate in the core MD02-2569 precipitated in or near isotopic equilibrium with present regional bottom water.

The carbonates in core MD02-2573GHF coexisted with pieces of gas hydrates in 4.2 mbsf sediments, close to the seafloor. Lacking of geothermal gradient value due to the core bent, we assume the nodule precipitated from temperature same as the bottom water (4.6 ^{o}C). Then the carbonates were calculated to have precipitated from water of

much heavier oxygen isotope $\delta^{18}O_w$ = +1.3‰ (Fig. 9, Table 2). However the core MD02-2573 is only 30 m away from the core MD02-2569.

Authigenic carbonates in the cores MD02-2570 and MD02-2571C2 occurred at 2.95 m and ~ 4.4 m in the sediments respectively, with a bottom water temperature of 6.5 ^{o}C, and the geothermal gradient of 36 ^{o}C/km. Then calculated in-situ temperatures of the carbonate-bearing sediments are all 6.6 ^{o}C. There is only 0.1 ^{o}C different from the bottom water temperature, which are negligibly small. Thus assuming the bottom water temperature 6.5 ^{o}C for the precipitated temperature of these carbonates, then the calculated $\delta^{18}O_w$ for the precipitated carbonates are +1.3 ‰ and +1.4 ‰ respectively, which are heavier than the present $\delta^{18}O_{sw}$ (Fig. 9).

In summary, the calculated $\delta^{18}O_w$ values for authigenic carbonates in the cores MD02-2546, 2573GHF, 2570 and 2571C2 are from +1.3 to 2.7 ‰, which are +0.5 to +1.9 ‰ higher than the present $\delta^{18}O$ value of *in-situ* bottom water/ pore water in the northern Gulf of Mexico. The possible sources for the ^{18}O-enriched water are (1) LGM (Last Glacial Maxium) northern Atlantic bottom seawater ($\delta^{18}O$ ~ +1.7 to +1.8 ‰) (Schrag et al., 2002), (2) deep-seated fossil brines ($\delta^{18}O$ > +3.0 ‰) (Gat, 1996), and (3) fluids from gas hydrates dissociation ($\delta^{18}O$ ~ +2.9 ‰) (e.g. Hesse and Harrison, 1981, Matsumoto, 1989).

The first option should be ruled out because the authigenic carbonates of this study precipitated in very recent time, younger than 5,500 yr ago. Then the bottom seawater $\delta^{18}O_{sw}$ will not be affected by the LGM bottom seawater oxygen isotope fractionation, and should be the same as the present measured values (+0.7 to +1.0 ‰).

As for the second possibility, some of the pore waters are observed to contain anomalously high Cl^- concentration from 1000 mM to up to 2161mM (Ussler and Paull, 2005), and however, their $\delta^{18}O_{IW}$ values are from -0.9 to +1.3‰, which indicate the high salinity pore waters do not carry water with an isotopic composition distinctive from seawater. These anomalously high salinity pore waters are not derived from the deep-seated brines, but from the simple dissolution of salts. Therefore the fossil brines' heavier $\delta^{18}O$ effect on the waters for these carbonate precipitation can also be excluded.

^{18}O-enriched carbonates might be related with gas hydrate dissociation have been reported for a number of cold seep environments worldwide (e.g., Matsumoto, 1989; Aloisi et al., 2000; Naehr et al., 2000; Pierre et al., 2000; Greiner et al., 2001). During the formation of gas hydrates from interstitial water, the water containing heavier oxygen isotopes are preferentially incorporated into the gas hydrate structure (Davidson et al., 1983; Matsumoto, 2000). Therefore gas hydrate decomposition liberates ^{18}O-enriched water molecules which can contribute between 1-2.9 ‰ to the ^{18}O enrichment of the interstitial waters (Hesse and Harrison, 1981).

Formation and decomposition of gas hydrates are observed to be ongoing in the northern GOM (Milkov and Sassen, 2003). These lines of evidence lead us to conclude that dissociation of pre-existing gas hydrate must have provided the ^{18}O-enriched water incorporated into the anomalously heavy ^{18}O in carbonates in the core MD02-2546 at the Tunica Mound, in the core MD02-2573GHF where carbonates coexisted with pieces of gas hydrates and in the core MD02-2570 and 2571C2 at the

Mississippi Canyon. Group II carbonates in the cores MD02-2546, 2570, 2571C2 were derived from microbial methane. All these carbonate are thus related to the dissociation of gas hydrate.

During the last 5,500 yr, it is clearly impossible that bottom seawater temperature increased or the sea level dropped to trigger the dissociation of gas hydrates associated with these cores MD02-2546, 2573GHF, 2570, and 2571C2. However the northern Gulf of Mexico is characterized by ongoing salt diapirism since Cenozoic. The salt movement has caused uplift of sediment layers and faulting/fracturing of sediments, which led to (1) decrease in geo-pressures of the associated gas hydrate hosting sediment horizons; (2) increase of pore water salinities of nearby sediments bearing gas hydrates. As a consequence, decomposition of gas hydrates was triggered in the associated sediment horizons. The seismic profile across the Tunica Mound (Fig. 2) clearly shows a large, shallow salt diapir existing nearby the core MD02-2546. The Cl^- concentrations of core MD02-2569, which is just 30 m away from core MD02-2573GHF, indicate a salt diapir underlying the core sediments (Ussler and Paull, 2005). The seismic profile across core MD02-2570 and 2571C2 (Fig. 4) shows gas chimneys in the sediments, which may also have been caused by the underlying salt upwarding. Thus we can conclude probably nearby salts/salt movement caused the dissociation of gas hydrates associated with these cores.

6. Summary and Conclusions

Carbonates sampled from various sub-depths in sediments at the Tunica Mound

and the Mississippi Canyon in northern Gulf of Mexico, are dominated by authigenic, micritic high Mg-calcites. The $\delta^{13}C$ values of carbonates indicate that these authigenic carboantes precipitated from DIC produced by microbially mediated anaerobic oxidation of methane.

The $\delta^{18}O$ values of carbonates indicate that some carbonates, including those from the core MD02-2569 with underlying massive gas hydrate, precipitated in or near equilibrium with present bottom-water; while the others including from the core MD02-2573GHF with underlying small pieces of gas hydrates precipitated from much ^{18}O-enriched fluids from the decomposition of gas hydrates, and away from equilibrium with present bottom-water/pore water. That is, authigenic carbonates at the cold seeps in the northern Gulf of Mexico, some are derived from the dissociation of gas hydrates, but some are only closely associated with methane venting probably from deep hydrocarbon gases. The dissociation of gas hydrates in the northern Gulf of Mexico within last 5,500 yr was probably caused by the salts/salt movement.

In a word, authigenic carbonates recorded the history of fluxes from gas hydrates in the Gulf of Mexico. The study on authigenic carbonates is probably a prosperous approach for gas hydrate research in other geologic settings, such as Nankai Trough.

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Figures:

Fig. 1. Coring locations of carbonates and pore water in northern Gulf of Mexico during July 2002 *Marion Dufresne* Cruise (MD-02). Carbonates were recovered from two areas – the Tunica Mound and the Mississippi Canyon.

Fig. 2. **Upper:** Seismic profile oriented NW-SE across the Tunica Mound seafloor area of Garden Bank Block 386 of the upper continental slope. Locations of cores containing carbonates are indicated with arrows. Note the underlying salt diapir and the well-defined faults which function as conduits for gas and fluids to migrate to the seafloor and has created a variety of vent-related features. **Lower:** Graphic logs shows the lithology, and distribution of carbonates in cores (C = carbonate nodules/crusts/hardgrounds; B = bivalves shell fragments)

Fig. 3. Specimens of carbonates in piston cores from theTunica Mound in the northern Gulf of Mexico.

Fig. 4. **Upper:** Seismic profile oriented NW-SE across west of the MC and central MC seafloor area at upper continental slope in the GOM. Locations of cores containing carbonates are indicated with arrows. **Lower:** Graphic logs show lithology,

and distribution of carbonates in cores (C = carbonate nodules/crusts/hardgrouds; B = bivalves shell fragments; H = gas hydrates)

Fig. 5. Specimens of carbonates from piston cores from the Mississippi Canyon in the northern Gulf of Mexico. A sample from the core MD02-2571C2 has a hole, probably as a gas conduit for upward migration of methane. Specimens of gas hydrates recovered in the cores MD02-2569 and 2573, and their photos were taken by W. Winters and T. Lorenson, respectively.

Fig. 6. Thin-section photomicrographs of carbonates. A: Micritic carbonates developed within silt-sized quartz grains (shining spots), framboidal pyrite (py) formed inside the cavities of formas (polarized light, sample MD02-2543G hardground). B: Bladed crystals of barite developed within the cavities around micritic calcites (polarized light, sample MD02-2544G porous nodule).

Fig. 7. Distribution of *d*(104) values for calcite of 31 authigenic carbonates.

Fig. 8. Carbon and oxygen isotopic compositions of carbonates from MD02 Cruise

Fig. 9. Calculated carbonate precipitated water oxygen isotopes. The blue shaded area represents present bottom water oxygen isotopes (+0.7 to +1.0 ‰). There is no specific vertical scale.

Tables:

Table 1. Chemical compositions of calcite in authigenic carbonates analyzed by electron microprobe analysis.

Table 2. Geological setting and results of isotopic and Mg^{2+} contents of carbonates, $\delta^{18}O$ values of interstitial water sampled from the upper 6 m of sediment cores, and calculated carbonate precipitated water oxygen isotopes

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